

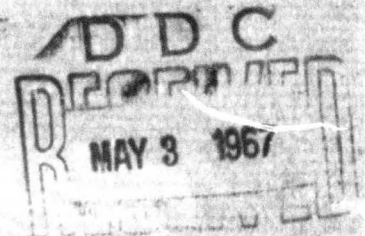
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RESEARCH PAPER P-311

THE EXCITATION OF ELECTRONIC AND
OTHER DEGREES OF FREEDOM IN A
HYPERSONIC SHOCK WAVE IN AIR

Ernest Bauer

January 1967



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I. INTRODUCTION

The aim of this report is to review our understanding of mechanisms for the excitation of electronic states of diatomic molecules in an actual non-equilibrium situation. Thus it complements the report by Gilmore, Bauer, and McGowan (1967), which surveys presently available excitation rates, by giving a worked example of a non-equilibrium situation in which excitation processes can actually be observed. Evidently, a normal shock furnishes the most extreme gas dynamic example of a non-equilibrium situation, and because of its technological importance, a great deal of work has been done on shock wave chemistry in air.

The present survey is directed as much to the chemists and physicists who study reaction rates and mechanisms as to the fluid mechanicians who study shock waves. It has been written to provide a minimum background of hypersonic shock structure, chemistry, and applications to non-specialists; it is an overall review of non-equilibrium phenomena in shock waves only insofar as the excellent reviews of Losev and Osipov (1961) and of Zel'dovich and Raizer (1963) reflect our understanding of 1961-1962 and have to be updated.*,** Accordingly, emphasis has been

*The Second Edition of Zel'dovich and Raizer's monograph (1966) is currently being translated by Hayes and Probstein and is to be published by Academic Press in 1967.

**For an overall survey of missile reentry, which provides an important application of hypersonic shock waves in air, the reader is referred to the excellent book by Martin (1966).

laid on presenting a simple and largely theoretical model. The references quoted here are to be regarded as representative rather than exhaustive, and throughout the report stress is placed on the limitations in the author's understanding of these matters.

The application which is reviewed here arises in the reentry of space vehicles into the terrestrial atmosphere. When a hypersonic vehicle traveling at perhaps 7 km/sec enters the earth's or some other planetary atmosphere, the gas in the "stagnation region," which is the blunt portion at the front of the vehicle, is brought to rest and its net flow velocity of $u_0 = 7$ km/sec is transformed into thermal excitation of the gas, raising the temperature of the gas to some value T_{stag} which depends rather drastically on both the value of u_0 and also on the nature of the gas.* As specific examples, we consider a normal shock in pure air for initial speeds $u_0 = 5$ and 7 km/sec, initially at room temperature and at an initial pressure $P_0 = 0.01$ atmospheres, corresponding to an altitude of approximately 30 km in the earth's atmosphere. Because air is rather a complicated medium, we also make comparison where appropriate with argon under equivalent conditions.

The outline of the report is the following: Section II presents the elements of shock wave theory and, in particular, the equilibrium energy balance before and after a normal shock in air and argon under the reference conditions, specifically the distribution of energy among

*The stagnation heating described in this way is essentially equivalent to the aerodynamic heating set up behind a normal shock.

different degrees of freedom. In fact, the approach adopted throughout this report--as is customary in this field--is to follow the flow of energy through translational, rotational, vibrational, chemical, and electronic degrees of freedom, with only a secondary emphasis on the specific chemical reactions. Section III discusses the coupling of energy between translational, rotational, and vibrational degrees of freedom, which is rather well understood, while Sec. IV discusses dissociation mechanisms, where there is a great deal of quantitative uncertainty. Section V presents a brief summary of the most important chemical reactions. Section VI is devoted to the well-studied and comparatively well-understood problem of ionization in both air and argon, while Sec. VII discusses the very limited and incomplete evidence that is presently available on the excitation mechanisms for electronic states of air molecules. Section VIII presents a preliminary model for electronic excitation processes in general, and Sec. IX gives a brief discussion of our understanding of the whole problem.

II. ENERGY BALANCE IN A NORMAL SHOCK

A normal shock is a one-dimensional gas flow in which ordered kinetic energy of hypersonic or at least supersonic motion of a gas* is transformed very rapidly** into random thermal energy, i.e., translational or internal, of the atoms or molecules that make up the gas. Thus, a shock is an adiabatic but irreversible process: The enthalpy is conserved but the entropy increases.

If a gas moves up stream of a shock with a high speed u_0 at a low temperature T_0 and low density ρ_0 , then downstream of the shock the gas moves at subsonic speed u_1 and specifically at a high temperature T_1 , and at a density $\rho_1 \lesssim 10 \rho_0$. For unit mass of gas, conservation of energy may be written as follows:

*A shock can only occur in supersonic flow because a signal in a gas propagates with the local speed of sound. If the flow is supersonic, the disturbance approaches a given volume so fast that the gas in the volume does not have time to react by moving away before the disturbance reaches it. Thus, there is a local "piling up" of gas which is called a shock. It is clear from this description that the flow pattern associated with a shock wave is irreversible. At 294°K the sound speed in air $a_0 = 0.33$ km/sec, while in argon at 294°K, $a_0 = 0.32$ km/sec, so that for the flows in question the Mach number $M_0 = u_0/a_0 \sim 15$ to 20 and thus the flow is described as "hypersonic," i.e., $M_0 \gg 1$.

**Instantaneously in the sense of a continuum gas flow model and, in fact, in 2 to 5 mean free paths.

$$(1-a) \quad \frac{1}{2} (u_0^2 - u_1^2) = h(T_1, \rho_1) - h(T_0, \rho_0) - \text{normal shock}$$

$$(1-b) \quad \frac{1}{2} u_0^2 = h(T_{\text{stag}}, \rho_{\text{stag}}) - h(T_0, \rho_0) - \text{stagnation heating}$$

where

$$(2) \quad h(T, \rho) = \int_0^T \left[C_p(T, \rho) / M(T, \rho) \right] dT$$

is the enthalpy per unit mass of the gas at temperature T and density ρ ; C_p is the specific heat per mole at constant pressure, and M is the effective molecular weight; both these quantities depend on both temperature and density because of the effect of dissociation, ionization, and internal excitation.

For a hypersonic situation $u_0/u_1 \gg 1$, so that $T_1 \approx T_{\text{stag}}$, and there is a very close correspondence between the heating of a gas in a normal shock and in a stagnation region. In fact, T_{stag} , as defined by Eq. 1-b, refers to the stagnation point at which all the kinetic energy of motion has been transformed into heat so that the gas has no flow velocity left. In the stagnation region as a whole, the gas does have a small flow velocity so that T_1 gives a better representation of the gas temperature than does T_{stag} . However, these are trivial refinements.

It is clear that for given values of u_0, T_0, ρ_0 (or P_0) and for a given equation of state, u_1, T_1, ρ_1 are determined. (Appendix A gives a brief account of this "Hugoniot" relation for a simple type of situation that can be treated analytically.)

There is a drastic difference in stagnation temperature produced for given values of u_0, T_0, ρ_0 in different gases under hypersonic conditions--say, $M_0 = u_0/a_0 \gtrsim 10$ --partly because of the internal degrees of freedom of rotation and vibration that are excited in diatomic as against monatomic gases, but largely because of the energy taken up in dissociating diatomic and polyatomic molecules and that taken up to ionize the various species. This can be seen very clearly in Tables 1 and 2 where we compare shock temperatures in air with those in argon and indicate, in particular, the energy budget for different degrees of freedom, all in an equilibrium situation.

It is clear that there is a drastic difference between monatomic and diatomic gases because the latter soak up large amounts of energy in dissociating. In fact, the richness and variety of physical and chemical phenomena that take place in molecular gases in the region from 2,000 to 10,000°K at normal pressures are due to the variety and significance of chemical and other inelastic processes that take place, giving rise to a number of different chemical species as well as to a host of different states of internal excitation. The various chemical and inelastic reactions that will be discussed here in outline present an example, which has been studied relatively intensively, of the interrelation of different reactions in high-temperature gases.

Table 1 -- ENERGY BALANCE BEHIND A NORMAL SHOCK IN AIR

$$P_0 = 0.01 \text{ atmosphere, } T_0 = 294^\circ\text{K}$$

A. $u_0 = 5 \text{ km/sec}$

Upstream of the Shock

Thermal enthalpy $c_p T_0$	= 0.006 ev/molecule
Directed kinetic energy, $1/2 M u_0^2$	= 3.76 ev/molecule

Downstream of the Shock

T_{stag}	= 5800°K ($\approx 0.5 \text{ ev}$)
Enthalpy of translational motion, $(5/2)kT$	= 1.25 ev/(atom or molecule)
Rotational enthalpy, kT	= 0.5 ev/molecule
Vibrational enthalpy	= 0.367 ev/molecule
Dissociation energy	= 1.507 ev/(atom or molecule)
Energy of electronic excitation ^a	= 0.13 ev/(atom or molecule)
Energy of ionization	= 0.002 ev/(atom or molecule)
Chemical energy ($N_2 + O_2 \rightleftharpoons 2 NO$)	= -0.02 ev/(atom or molecule)

Equilibrium Composition Downstream of the Shock^b

$[N_2]$	7.29^{-1}	$[e^-] = [NO^+]$	1.6^{-4}
$[NO]$	2.05^{-2}		
$[O_2]$	1.26^{-3}		
$[N]$	9.85^{-2}		
$[O]$	4.00^{-1}		

B. $u_0 = 7 \text{ km/sec}$

Upstream of the Shock

Thermal enthalpy $c_p T_0$	= 0.006 ev/molecule
Directed kinetic energy, $1/2 M u_0^2$	= 7.3 ev/molecule

Downstream of the Shock

T_{stag}	= 7500°K ($\approx 0.647 \text{ ev}$)
Enthalpy of translational motion $(5/2)kT$	= 1.62 ev/(atom or molecule)
Rotational enthalpy, kT	= 0.65 ev/molecule
Vibrational enthalpy	= 0.512 ev/molecule
Energy of dissociation	= 4.17 ev/(atom or molecule)
Energy of electronic excitation	= 0.17 ev/(atom or molecule)
Energy of ionization	= 0.01 ev/(atom or molecule)
Chemical energy ($N_2 + O_2 \rightleftharpoons 2 NO$)	= -0.01 ev/(atom or molecule)

Equilibrium Composition Downstream of the Shock

$[N_2]$	4.62^{-6}	$[NO^+]$	8.06^{-4}
$[NO]$	9.46^{-3}	$[N^+]$	1.82^{-4}
$[O_2]$	1.92^{-4}	$[O^+]$	1.04^{-4}
$[N]$	6.38^{-1}	$[e^-]$	1.14^{-3}
$[O]$	4.13^{-1}		

^aFor simplicity, we assume that every atom or molecule has an electronic state 1 ev above the ground state and of statistical weight equal to that of the ground state.

^b $7.29^{-1} = 7.29 \times 10^{-1}$, etc.

Table 2 -- ENERGY BALANCE BEHIND A NORMAL SHOCK IN ARGON

$P_0 = 0.01$ atmosphere, $T_0 = 294^\circ\text{K}$

A. $u_0 = 5$ km/sec

Upstream of the Shock

Mean kinetic energy, $1/2 M u_0^2 = 5.2$ ev/atom

Downstream of the Shock

$T_{\text{stag}} = 13,000^\circ\text{K}$ (≈ 1.12 ev); $[\text{Ar}] = 0.875$; $[\text{Ar}^+] = [\text{e}^-] = 0.125$

Enthalpy of translational motion, $(5/2)kT = 2.80$ ev

Energy of ionization $= 1.98$ ev/(atom or ion)

Energy of electronic excitation $= 4 \times 10^{-4}$ ev/(atom or ion)

B. $u_0 = 7$ km/sec

Upstream of the Shock

Mean kinetic energy $= 10.2$ ev/atom

Downstream of the Shock

$T_{\text{stag}} = 15,700^\circ\text{K}$; $[\text{A}] = 0.648$; $[\text{A}^+] = [\text{e}^-] = 0.351$

Energy Balance Downstream of the Shock

Enthalpy of translation per particle, $(5/2)kT = 3.4$ ev

Ionization energy per particle $= 5.5$ ev

Electronic excitation energy per atom $\approx 2.10^{-3}$ ev

III. COUPLING OF TRANSLATION, ROTATION, AND VIBRATION

In Sec. II, we discussed the equilibrium distribution of energy before and after a shock, but now we proceed to ask the more detailed question of how the energy passes from directed kinetic energy corresponding to rectilinear flow with velocity u_0 into the thermal equilibrium excitation listed in Tables 1 and 2.

Let us first consider the case of argon, where atoms moving with a velocity u_0 , corresponding to a kinetic energy of 5 to 10 ev, strike room temperature argon atoms whose effective random kinetic energy is $(3/2)kT_0 = 0.04$ ev. The transfer of kinetic energy in a collision between two argon atoms is very efficient, and in a one-dimensional situation an argon atom goes from a kinetic energy of 10 to 1.3 ev (the new equilibrium value) in three collisions. Since the motion is not rectilinear, we may allow perhaps an equal number of collisions for the direction of the velocity to be randomized, making a total of 5 to 10 collisions. It is not difficult to understand the experimental measurements--e.g., Camac (1963); Robben and Talbot (1966)--which show the thickness of a hypersonic shock front in argon to be of the order of 5 mean free paths; the Monte Carlo calculations of Alder and Wainwright (1958) confirm this result by computer simulation.

In the case of a molecular gas (other than hydrogen), the rotation, but not the vibration, is, in general, closely coupled to the translation;

typically, it takes 3 to 5 collisions to equilibrate translation and rotation--cf. Losev and Osipov (1961), Lawley and Ross (1965). Thus, one would expect the translation and rotation to relax together, and indeed this is observed; for instance, Camac (1963) finds that in N_2 at $M_0 \sim 3-10$ the shock thickness and structure are comparable to that in argon, showing that the rotation is closely coupled to the translation. In a hypersonic shock wave there is an initial "overshoot" in the rotational and translational temperature. In a very few collisions all the energy of motion goes into the translational and rotational degrees of freedom, yielding a maximum temperature T_{\max} given by

$$(3) \quad (5/2) kT_{\max} = \frac{1}{2} M u_0^2$$

where M is the mass of an undissociated air molecule; thus for $u_0 = 7$ km/sec, $T_{\max} = 24,000^\circ K$. This overshoot has been observed--cf. Allen (1965).

In contrast to the rotation, which is closely coupled to the translation, it is well known that the vibration is very weakly coupled to the translation, at least in room temperature gases--cf. Massey and Burhop (1952), pp. 454ff. Thus, at room temperature the number of collisions Z_{vib} required to excite one vibrational quantum lies in the range 10^4 to 10^8 ; at the elevated temperatures existing behind a hypersonic shock, Z_{vib} is much smaller, but still $Z_{vib} \sim 10^3$ is quoted as a representative number--cf. Losev and Osipov (1961). The basic reason for this is that the characteristic frequency $\nu_e \sim 6 \times 10^{13}$ c/sec of a

vibration is very large compared to the characteristic frequency for a gas kinetic collision, $1/t_{\text{coll}} \sim u/d$, where u (≈ 1 km/sec) is a mean thermal speed and $d \approx 3 \times 10^{-8}$ cm is the approximate range of interatomic forces, so that $1/t_{\text{coll}} \sim 3 \times 10^{12}$ c/sec. As a result of this discrepancy of characteristic frequencies of the perturbing force and of the molecule system, the probability of excitation is very low. Some further comments on the vibrational relaxation process are given in Appendix B.

In fact, this picture of the shock structure does not hold up to the rather high speeds that are under consideration here. Thus, for oxygen at an initial pressure $P_0 = 2-4 \times 10^{-5}$ atmospheres, Wray and Freeman (1964) find that at about $M_0 = 10$ ($u_0 = 3$ km/sec) the vibrational excitation begins to appear in the same zone as translational and rotational excitation; by $M_0 = 14$ ($u_0 = 4.2$ km/sec) these three processes appear together, and around $M_0 = 16$ ($u_0 = 4.8$ km/sec) dissociation starts to occur in the same zone.* It is clear that we cannot separate the excitation of the various degrees of freedom at these high energies, at which vibrational excitation occurs, in part, by impulsive collisions--cf. Mies and Shuler (1962), Rapp and Sharp (1963), and, in part, as a result of chemical reactions--cf. Bauer and Tsang (1963), perhaps, of the type



Some of these points are discussed in Appendix B.

*It must be stressed that the conditions referred to in oxygen are significantly more extreme than the reference conditions in air of Table 2; O_2 is fully dissociated at a much lower temperature than air, especially at the very low densities of these experiments. At 4000°K, O_2 is fully dissociated in equilibrium for $\rho/\rho_0 = 10^{-4}$, while air is equally fully dissociated at $\rho/\rho_0 = 10^{-2}$ at perhaps 9000°K.

IV. THE INTERACTION OF VIBRATIONAL EXCITATION AND DISSOCIATION

Thus far, we have discussed how the directed kinetic energy of the hypersonic flow, $\frac{1}{2} M u_0^2$ per molecule, is transformed into random kinetic energy (i.e., thermal energy) of the molecules behind the shock, and how it is transformed in part into rotational and vibrational excitation. We now turn to chemical excitation per se: We see from Table 2 that in our situation the heat of dissociation of the N_2 and O_2 molecules takes up the largest part of the initial energy. Here we discuss in general terms the mechanisms by which the dissociation takes place, leaving for the next Section a discussion of the problem from a rather different viewpoint, in which attention is focused on the chemical species rather than on the transfer of energy.

It is generally considered that dissociation takes place by "climbing the vibrational ladder"; that is, a molecule in a series of collisions is excited successively into higher and higher vibrational states until it finally dissociates.*

*It should be pointed out that there is also the possibility of dissociation by rotational excitation (Bauer, 1958), and more generally the probability that vibrational ladder-climbing actually involves simultaneous rotational and vibrational excitation--see also Bauer and Tsang (1963). In fact, these suggestions of the possible importance of rotational excitation have never been investigated in detail.

At least for the lower vibrational levels v , successive collisions produce changes $\delta v = \pm 1$ in the vibrational quantum number; as v increases the spacing $\delta E_v = E_{v+1} - E_v$ decreases, and transitions involving $\delta v = \pm 2, \pm 3, \dots$ become more important. As is implicit in the nature of this process, the ladder-climbing is not monotonic but rather of the nature of a random walk or diffusion process--cf. Montroll and Shuler (1958); and while at the lower vibrational levels a discrete analysis of the ladder-climbing process is appropriate--cf. Montroll and Shuler (1958)--yet at the higher levels of excitation, near the dissociation limit, the vibrational levels are so closely spaced that a continuous model is more appropriate--cf. Widom (1963), Keck and Carrier (1965), and Brau, Keck and Carrier (1966).

If z_v is the occupation probability of the v -th vibrational level $q_{v,v'}$ ($v' > v$) is the $(v \rightarrow v')$ excitation probability, then the "bottle-neck" or rate-limiting level v_R is characterized roughly by the condition

$$(5) \quad \left\{ \begin{array}{l} Q(v) = z_v(T) \left\{ \sum_{v' > v} q_{v,v'} - \sum_{v'' > v} q_{v'',v} \right\} \\ \quad = \text{minimum as a function of } v \text{ for } v = v_R \end{array} \right.$$

where

$$(6) \quad z_v(T) \sim g_{J(v)} e^{-E_v/kT}$$

and where $g_{J(v)}$ = rotational statistical weight corresponding to the v -th vibrational level. The transition probability $q_{v,v'}$ is actually rather a complicated function of v, v' as well as of the effective

temperature or kinetic energy of collision, and also of the colliding species. Thus, for v small and low energy collisions, $q_{0,1}$ is the smallest of all the $q_{v,v+1}$ and the $q_{v,v+\delta v}$ ($\delta v > 1$) are all very small--cf. Bauer and Cummings (1962); in the opposite limit of v large and a large kinetic energy of impact all the $q_{v,v'}$ become large, including those with $\delta v > 1$ --cf. Mies and Shuler (1962), and Rapp and Sharp (1963).

In addition to the rather refined analyses of Montroll and Shuler (1958), Widom (1963), Osipov and Stupochenko (1963), and that of Keck and Carrier (1965), the last of which has complete lists of references to other works in this field, note should also be made of the work of Rice (1961, 1963) for its comprehensive statement of the problem, and to the simple, semi-empirical but useful "CVD" ("coupled vibration and dissociation") model of Hammerling, Teare and Kivel (1959). It is clear that the efforts of these and other workers in the field have provided an overall description of the general character of the problem at not too high a temperature, but all these calculations have severe limitations if one asks for a quantitative a priori prediction of the dissociation rate for a given situation.

Measurements of shock front structure in pure oxygen due to Wray and Freeman (1964) show that the picture outlined in Sec. III and IV does indeed apply at low temperatures and flow speeds (perhaps $T \lesssim 4000^\circ\text{K}$, $u_0 \lesssim 3.6$ km/sec in air at $P_0 \approx 0.01$ atmospheres). Energy from ordered translation flows very rapidly into random translation and rotation, then rather slowly into the lower vibrational levels, and after that by a diffusive process of "vibrational ladder-climbing"

into dissociation. However, at the higher temperatures and flow speeds considered here, this model certainly does not hold in its totality. Wray and Freeman (1964) find that for pure oxygen at $P_0 \sim 10^{-5}$ atmospheres near $u_0 = 4.2$ km/sec, the vibrational excitation occurs in the same zone as translational and rotational equilibration, while around $u_0 = 5.6$ km/sec, dissociation begins to occur in the same zone as rotational and vibrational excitation. If one projects these results to the case of air at $P_0 \approx 0.01$ atmospheres on a basis of equal degrees of dissociation, then around $u_0 \sim 7$ to 8 km/sec dissociation might be expected to occur simultaneously with rotational and vibrational equilibration. It is clear that under these extreme conditions* the present orderly model has broken down completely, since now energetic and "impulsive" collisions excite the vibration and rotation many steps at a time, while chemical processes involving rearrangement of atoms will contribute to the vibrational (and rotational, and possibly even electronic) excitation.

*It must be stressed that the conditions referred to in oxygen are significantly more extreme than the reference conditions in air of Table 2; O_2 is fully dissociated at a much lower temperature than air, especially at the very low densities of these experiments. At $4000^\circ K$, O_2 is fully dissociated in equilibrium for $\rho/\rho_0 = 10^{-4}$, while air is equally fully dissociated at $\rho/\rho_0 = 10^{-2}$ at perhaps $9000^\circ K$.

V. CHEMICAL REACTIONS IN A HYPERSONIC SHOCK IN AIR

It is clear from the preceding discussion that a large number of chemical species are formed in a strong shock wave in air, and that the formation of these species proceeds through a complicated series of reactions involving the excitation of various internal degrees of freedom. Briefly, first the translational and rotational degrees of freedom are excited, then the vibrational levels are excited; in parallel with this, the oxygen and then the nitrogen molecules dissociate. As soon as there are some free atoms present, a number of atom interchange reactions take place and then ionization occurs through atom-atom inelastic processes, conventionally represented by



The overall chemistry proceeds through an exceedingly complicated set of reactions; a simplified version incorporating just six reaction pairs is indicated as processes (7) to (12) in Table 3. These high-temperature reaction rates come from shock tube experiments in this temperature-density range and are optimized by means of a computer simulation at AVCO-Everett Research Laboratory. Figures 1-a and 1-b show the variation of species concentrations as a function of time or distance through the shock computed by this non-equilibrium chemistry code.

Table 3 -- A SIMPLIFIED SET OF CHEMICAL REACTIONS
FOR HIGH-TEMPERATURE AIR (Bortner 1966)

Reactions ^d		Rate Constants ^b						
A. Dissociation and Recombination		Reaction	Forward			Reverse		
(8)	$O_2 + M \rightleftharpoons O + O + M$	M = O ₂	5.4 (-5)	-1	59.4	1.5 (-32)	-1/2	0
		O	1.5 (-4)	-1	59.4	2.1 (-31)	-1/2	0
		N ₂	1.2 (-5)	-1	59.4	1.7 (-32)	-1/2	0
		N, NO, Ar	6.0 (-6)	-1	59.4	8.3 (-33)	-1/2	0
(9)	$N_2 + M \rightleftharpoons N + N + M$	M = N ₂	7.9 (-7)	-1/2	113.1	7.3 (-32)	-1/2	0
		N	6.9 (-2)	-3/2	113.1	6.4 (-27)	-3/2	0
		O ₂ , O, NO, Ar	3.2 (-7)	-1/2	113.1	3.0 (-32)	-1/2	0
(10)	$NO + M \rightleftharpoons N + O + M$	M = NO, O, N	1.3 (-2)	-3/2	75.6	5.4 (-27)	-3/2	0
		M = O ₂ , N ₂ , Ar	6.6 (-4)	-3/2	75.6	2.8 (-28)	-3/2	0
B. Exchange Reactions								
(11)	$O + NO \rightleftharpoons N + O_2$		5.3 (-15)	1	19.7	1.6 (-12)	1/2	3.6
(12)	$O + N_2 \rightleftharpoons N + NO$		1.12 (-10)	0	37.5	2.1 (-11)	0	0
C. Ionization and De-Ionization at High Temperatures								
(13)	$N + O \rightleftharpoons NO^+ + e^-$		1.5 (-14)	1/2	32.4	3.0 (-4)	-1	0
D. Electron Disappearance at Low Temperatures: Negative Ions								
(13')	$O_2 + e^- \rightleftharpoons O_2^- + M$	M = O ₂	1.4 (-31)	1/2	0	4.0 (-16)	2	5.1
		N ₂	5.8 (-33)	1/2	0	1.7 (-17)	2	5.1
		O	1.7 (-33)	1/2	0	5.6 (-18)	2	5.1
(14)	$O_3 + e^- \rightleftharpoons O^- + O_2$		3.0 (-12)	0	0			
(15)	$O_2^- + O \rightleftharpoons O_3 + e^-$		3.0 (-10)	0	0			
(16)	$O_2^- + O \rightleftharpoons O^- + O_2$		1.0 (-11)	0	0			

^aReactions (7-12) provide a consistent overall picture for $T \geq 2000^\circ K$; at lower temperatures NO₂ has to be considered as well as O₃, since both may be important minor species in determining the cleanup of free electrons. Reactions (13-16) are given to indicate some of the complexities of negative ion chemistry. See Bortner (1966) for a consistent set of low temperature reactions.

^bRate constants are given by three numbers which are a, b, c, respectively, in the expression $k = a T^b e^{-10^3 c/T}$. The values of "a" are given by two numbers, the second (in parentheses) being the power of ten by which the first is to be multiplied. Thus, 3(-10) represents 3×10^{-10} . The units are such that the concentrations are to be expressed in particles cm^{-3} .

It must be stressed that the set of reaction rates of Table 3 provides merely a heuristic scheme for explaining approximately a very large volume of experimental data with a minimum number of parameters. Explicitly, this set of reaction rates accounts roughly for the energy balance and also for the ionization and de-ionization at elevated temperatures. The reaction rates do not refer explicitly to the internal excitation and, thus, cannot account for the optical radiation; they also omit impurities such as sodium, which can be very important for ionization, and minor species, such as CO_2 , H_2O , NO_2 , CN , etc., which can be very important for the radiation from pure air. The negative ion reactions (13) to (16) of Item D in Table 3 are shown merely to indicate some of the complications that arise when one tries to extend the model to lower temperatures; the point is that once we begin to deal with minor species, matters can become extremely complicated.

VI. IONIZATION AND DE-IONIZATION IN HIGH-TEMPERATURE GASES

When one discusses ionization and de-ionization in the present range of energy and mass densities, there is a drastic difference between monatomic and diatomic species. In the former case, ionization provides a very important sink for energy, whereas in the latter case ionization is merely a minor perturbation from the standpoint of energy balance, since dissociation takes up the bulk of the energy. This may be seen by comparing Tables 1 and 2, and the implications of this difference show up also when one asks for optical excitation.

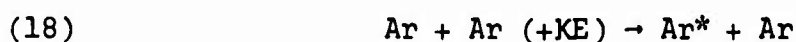
A. ARGON

Here ionization provides a very important mechanism for the absorption of energy. The principal mechanism for ionization is provided by electron impact



but evidently this mechanism only becomes operative once a sufficient number of free electrons have been produced by some other mechanism, and if there exists a mechanism for "heating" the free electrons to provide the necessary ionization energy of 15.8 ev.

The mechanism for the initial part of the ionization differs somewhat in different energy ranges. At relatively low shock speeds ($\lesssim 3$ km/sec), it has been established that the initial ionization takes place by a two-step process:



where * denotes electronic excitation; the excitation step (18) is, in general, the rate-limiting step--cf. Petschek and Byron (1957), and Kelly (1966). At higher speeds in particular, there is a significant amount of precursor ionization produced by the absorption of ultraviolet radiation emitted from electronically excited argon atoms.* Evidently in this situation the excitation step (18) is once again crucial, but because of the complicated chain of processes leading to ionization it is not clear what is the rate-limiting step. The mechanism for "heating up" the free electrons is provided by elastic collisions of electrons with Ar^+ ions and Ar atoms--cf. Petschek and Byron (1957).

As an example of a system of argon with metallic additives, reference may be made to the work of Shackleford and Penner (1966) who study the ionization mechanism of chromium in Ar-Cr mixtures in a shock

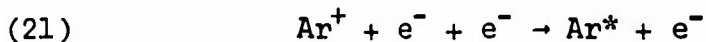
The calculations of Biberman and Veklenko (1959) show that 1 meter ahead of a shock of speed $u_0 \approx 5.5$ km/sec at $P_0 = 10^{-2}$ atmospheres in argon, the excitation temperature (given by the ratio of concentrations of Ar^ to Ar) is 13,500°K, almost equal to the quoted equilibrium temperature of 14,000°K behind the shock.

tube at a temperature of about 7000°K. The ionization mechanism is complex. First of all Cr is excited by collision with electrons and/or atoms to electronic levels approximately 3.1 ev above the ground state; excitation to higher excited levels is fast, and finally ionization occurs from electronically excited states of Cr by rate-determining processes that involve inelastic collisions with electrons or atoms.

Recombination, i.e., de-ionization,* occurs at high temperatures ($T \gtrsim 10,000^\circ\text{K}$) by collisional-radiative recombination--cf. Bates and Dalgarno (1962)--which is a complex process tending toward radiative recombination



in the low-density limit and to three-body recombination

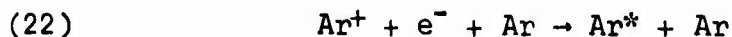


in the high-density limit. In fact, under the conditions of interest here in which the plasma is only partially ionized, there are a number of complicating factors:

1. In the three-body electron-electron-ion recombination process (21), the rate-limiting step is apparently not the recombination step but the rate at which the free electrons lose their energy, i.e., "are cooled," presumably by elastic collisions with Ar^+ ions and also with Ar atoms.

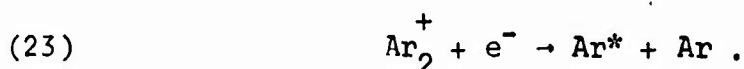
*The word "recombination" is used both for electron-ion recombination and for atom-atom recombination, and confusion sometimes arises.

2. The electron-ion-atom three-body recombination process



is also important under the present conditions.

3. At room temperature, it appears that the dominant positive ion is Ar_2^+ , and recombination occurs by the very fast process of dissociative recombination--cf. Frommhold and Biondi (1966).



It must be stressed that this discussion does not claim to be complete or comprehensive. The reason for presenting it is to indicate some of the components of the story and to demonstrate how complicated things can get even in a situation as simple as in a noble gas. Evidently in the case of air, which is a mixture of diatomic species, one would expect an even greater wealth of contributing phenomena, and a very brief survey of this is now given.

B. AIR

It is clear that to give a detailed account of the ionization mechanisms in air is a very tedious and involved matter, but the physics of the process can be understood in overall terms by means of three hypotheses:

1. In air under reentry conditions most of the energy from the shock wave goes into breaking bonds (dissociating the O_2 and N_2 molecules), and one would expect a minor perturbation like ionization to

proceed by "feeding" on the main available supply of excitation, by using the atoms that have already been produced.

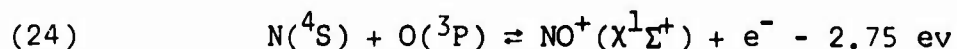
2. In fact, of all the species present in equilibrium air at temperatures of 2000 to 8000°K, NO has the lowest ionization potential: 9.25 ev against 12.05 ev for O₂; 13.62 for O, 14.55 for N, and 15.58 ev from N₂--cf. Gilmore (1955). Thus, if any other molecular or atomic ions are formed they will quickly undergo charge transfer or ion-atom interchange to give NO⁺.

3. At temperatures below 2000°K, several negative ions such as NO₂⁻, O⁻, O₂⁻, O₃⁻ with an electron affinity of the order of 0.5 ev--cf. Moiseiwitsch (1965)--become an important trap for the relatively few remaining free electrons, giving rise to a whole new class of reactions involving minor species and negative ions. A representative subset of these reactions is shown as Item D of Table 3, i.e., as processes (13) and (16).

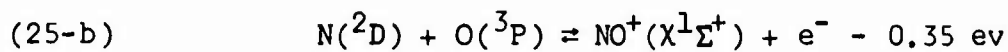
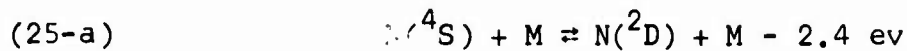
Bearing these three remarks in mind, it is clear that the dissociative recombination process



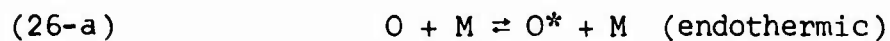
which is listed as the main ionization-deionization step for $T \gtrsim 3000^\circ\text{K}$, is in fact merely representative of a large and rather complex class of reactions. Thus, we can write (7) as



yet the cycle



may well be an important contributor to the ionization-deionization process, as may some cycle such as



At the lower temperatures where triatomic molecules and also negative ions contribute, things become a great deal more complicated as is indicated by the example of Eqs. (13) and (16) in Table 3. That part of the story is not yet fully understood, although it is under detailed investigation at present.

VII. EXCITATION OF ELECTRONIC STATES BEHIND SHOCK WAVES: EXPERIMENTAL EVIDENCE

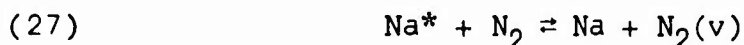
A very substantial effort has been devoted to understanding the kinetics of dissociation and ionization of air in shock waves. As a result of this large effort we now have at least an overall and semi-quantitative understanding of these phenomena, although, as the preceding discussion has indicated, there are really significant gaps in our overall understanding of the detailed physical processes involved. However, the question, how do air molecules get excited into states which then radiate?, has not been resolved in a comparably detailed and satisfactory way. There are several reasons for this state of affairs:

1. Technologically the problem of excitation mechanisms and rates for electronic states has not proved to be an important one because air radiation is not an important mechanism for reentry heating for incident velocities of the order of 7 km/sec or less. (A very brief discussion of air radiation is given in Appendix C.)

2. The available evidence indicates that excitation of electronic states is rather fast and quite complex, making the problem of elucidating the excitation mechanisms a fairly difficult one that is not particularly rewarding in a technological sense.

The available experimental evidence is not very complete.

(a) Examination of the Na-D line radiation arising from an impurity of sodium behind shock waves in nitrogen at temperatures of 1700 to 4300°K shows that the radiation follows the vibrational temperature of molecular nitrogen (Hurle, 1964). This can be understood at least qualitatively because it is known that both the forward and the backward reactions



are fast--cf. Tsuchiya and Kuratani (1964), and Starr (1965).

(b) A preliminary analysis of the total light emitted when particles are flown in a hypervelocity gun range in air (Hansen and Chapin, 1964) indicates that as both flight speed (or stagnation temperature) and pressure are varied, the assumption

$$(28) \quad T_{\text{elec}} \approx T_{\text{trans}}$$

is adequate at $P = 1$ atmosphere but breaks down at lower pressures; the assumption

$$(29) \quad T_{\text{elec}} \approx T_{\text{vib}}$$

holds to significantly lower pressures ($P \gtrsim 10^{-2}$ atmospheres), but yet a better fit to the data is obtained on the assumption that excitation occurs by two-body collisions with both electrons and neutral particles:



(c) Limited experiments on N_2 in a shock tube are shown in Fig. 2 (Allen, 1965), where a spectroscopic technique is used to measure rotational, vibrational, and electronic temperature histories for an incident nitrogen shock. The rotational and vibrational temperatures were obtained from the $N_2^+(1-)$ band system, so that they refer to the rotational and vibrational temperature of $N_2^+(B^2\Sigma_u^+)$ rather than to those of $N_2(X^1\Sigma_g^+)$. Since we do not know the excitation mechanism of $N_2^+(B)$, it is not evident that these rotational and vibrational temperatures apply also to $N_2(X)$, and, in fact, it is almost certain that they do not. The electronic temperature is obtained from the $N_2(1+)$ band system, so that it refers to the relative population of $N_2(B^3\Sigma_u^+)$ and $N_2(X)$.

If one carries out a reaction rate calculation for pure N_2 analogous to the results for air of Fig. 1, it appears* that the characteristic time for dissociation under these conditions is of the order of 10^{-7} sec, which is just the time at which the electronic temperature has its maximum.

*At the time of writing this I do not have these reaction rate calculations; I am merely scaling the density dependence of the results of Fig. 1 and allowing for the fact that N_2 chemistry is somewhat slower than air chemistry. Such calculations should be carried out.

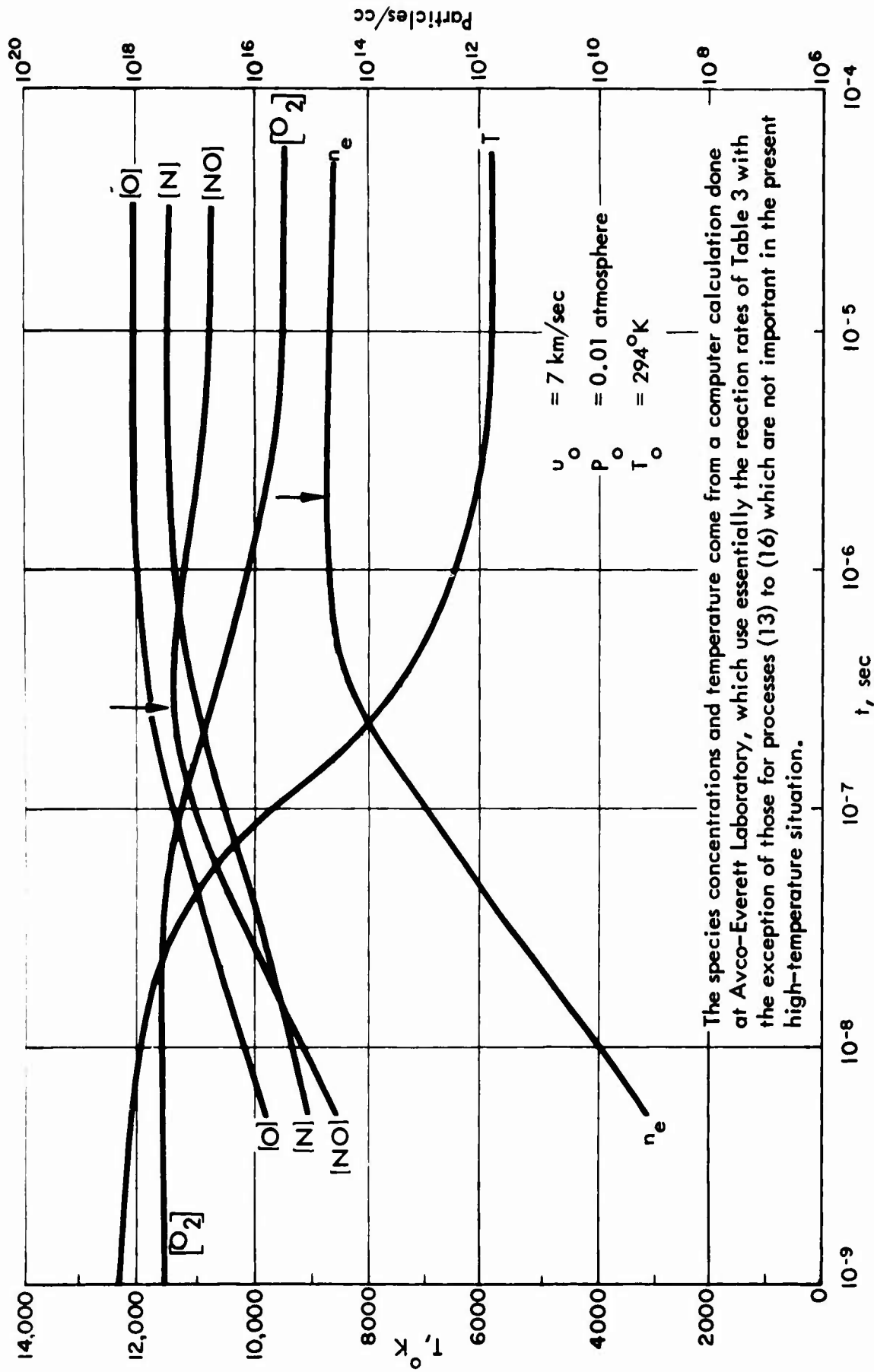


FIGURE 1-a Chemical Reactions Behind a Shock Front in Air ($u_0 = 5 \text{ km/sec}$)

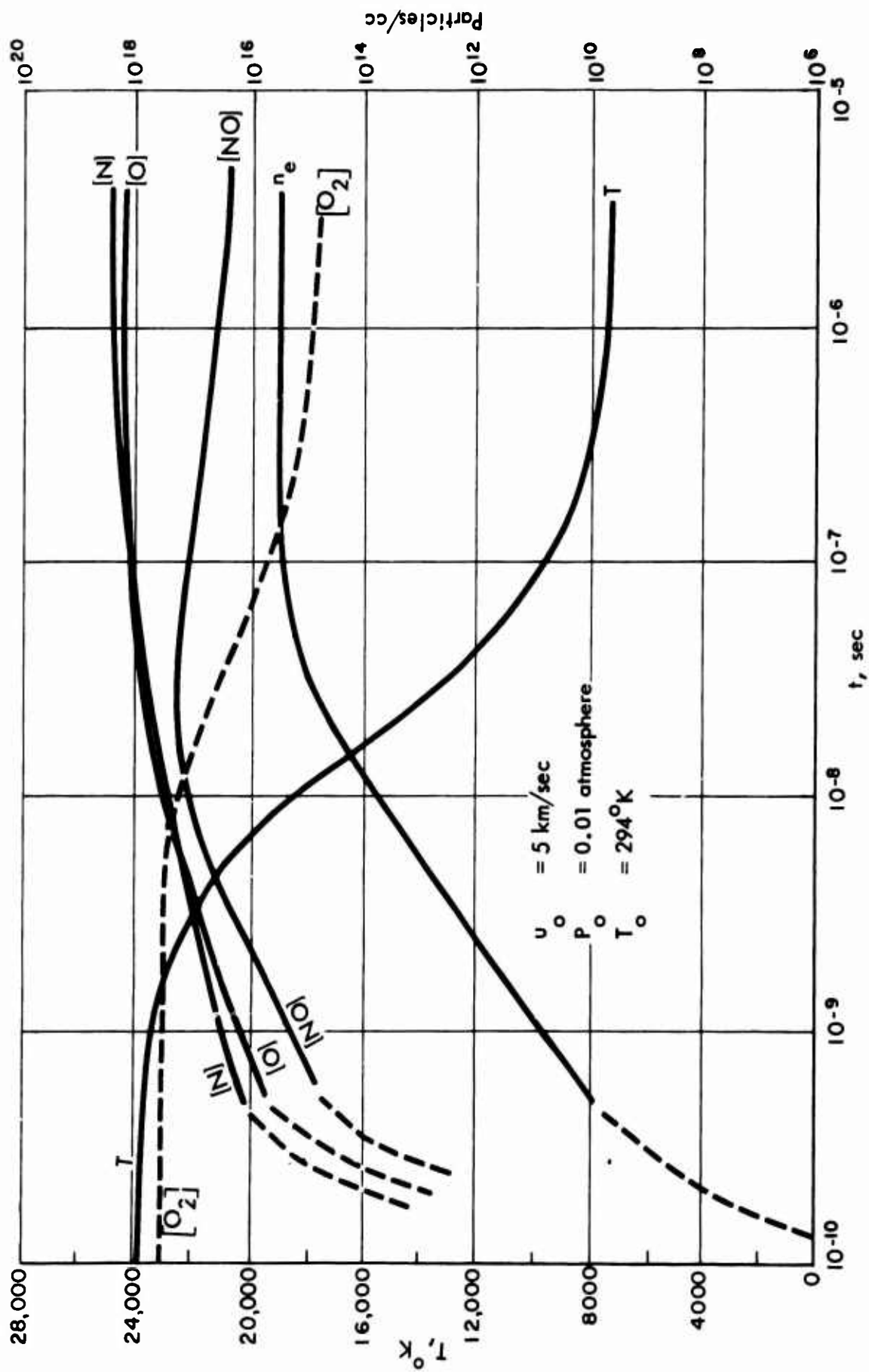
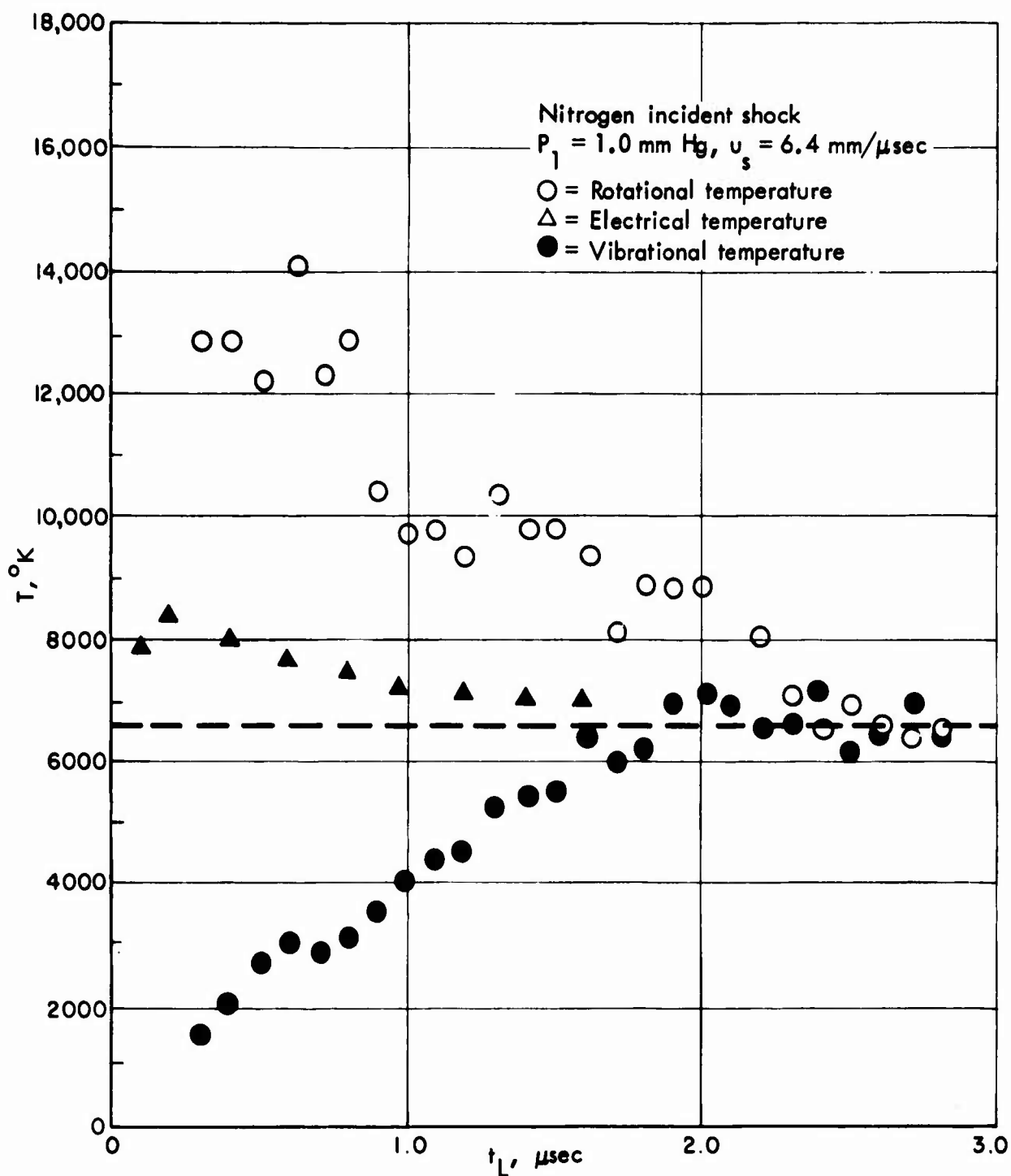


FIGURE 1-b Chemical Reactions Behind a Shock Front in Air ($u_0 = 7 \text{ km/sec}$)



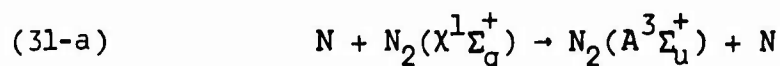
The rotational and vibrational temperatures refer to the $\text{N}_2(\text{B}^2\Sigma_u^+)$ state and it is by no means apparent that they also refer to the ground state $\text{X}^1\Sigma_g^+$ of N_2 . See Item (c) of Section VII for a discussion of these results.

FIGURE 2 Measured Rotational, Vibrational, and Electronic Time Histories for an Incident Shock in Nitrogen (Allen, 1965)

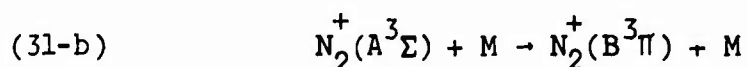
From this fact one infers

1. that the assumption on chemi-excitation of $N_2(B)$ is consistent with the data,
2. that presumably the vibrational excitation of $N_2(X)$ tracks the dissociation of N_2 , so that it is at least ten times faster than the vibrational excitation of $N_2^+(B)$, and
3. that it is very hard to understand the magnitude of the rotational overshoot unless one invokes some rather specific characteristics for the rotational excitation of $N_2^+(B)$.

(d) Experimental work on N- N_2 mixtures in shock tubes (Wray, 1966) indicates that for excitation of the $N_2(1+)$ band system, at temperatures above 7000°K the rate-limiting step involves an atom exchange reaction

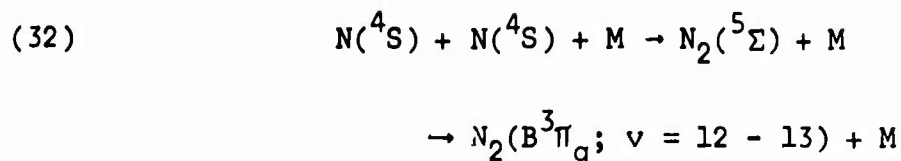


followed by the fast reaction



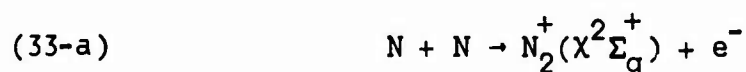
which is in equilibrium.

This is in considerable contrast to the model (Kistiakowsky and Warneck, 1957) of three-body recombination of two $N(^4S)$ atoms into the shallow $N_2(^5\Sigma)$ state which then undergoes an electronic transition by "potential energy curve crossing" into the bound state $N_2(B^3\Pi_g)$, near vibrational level $v = 12$ to 13

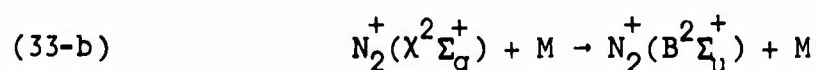


--cf. Fig. 3 (Gilmore, 1965). This model is generally accepted as applying in glow discharges and at temperatures up to perhaps 2000 to 3000°K. For related work, see Young and Sharpless (1963), and Wentink, Sullivan and Wray (1958).

(e) For $N_2^+(1-)$, Wray (1966) suggests tentatively that the rate-limiting step is associative ionization of N-atoms,



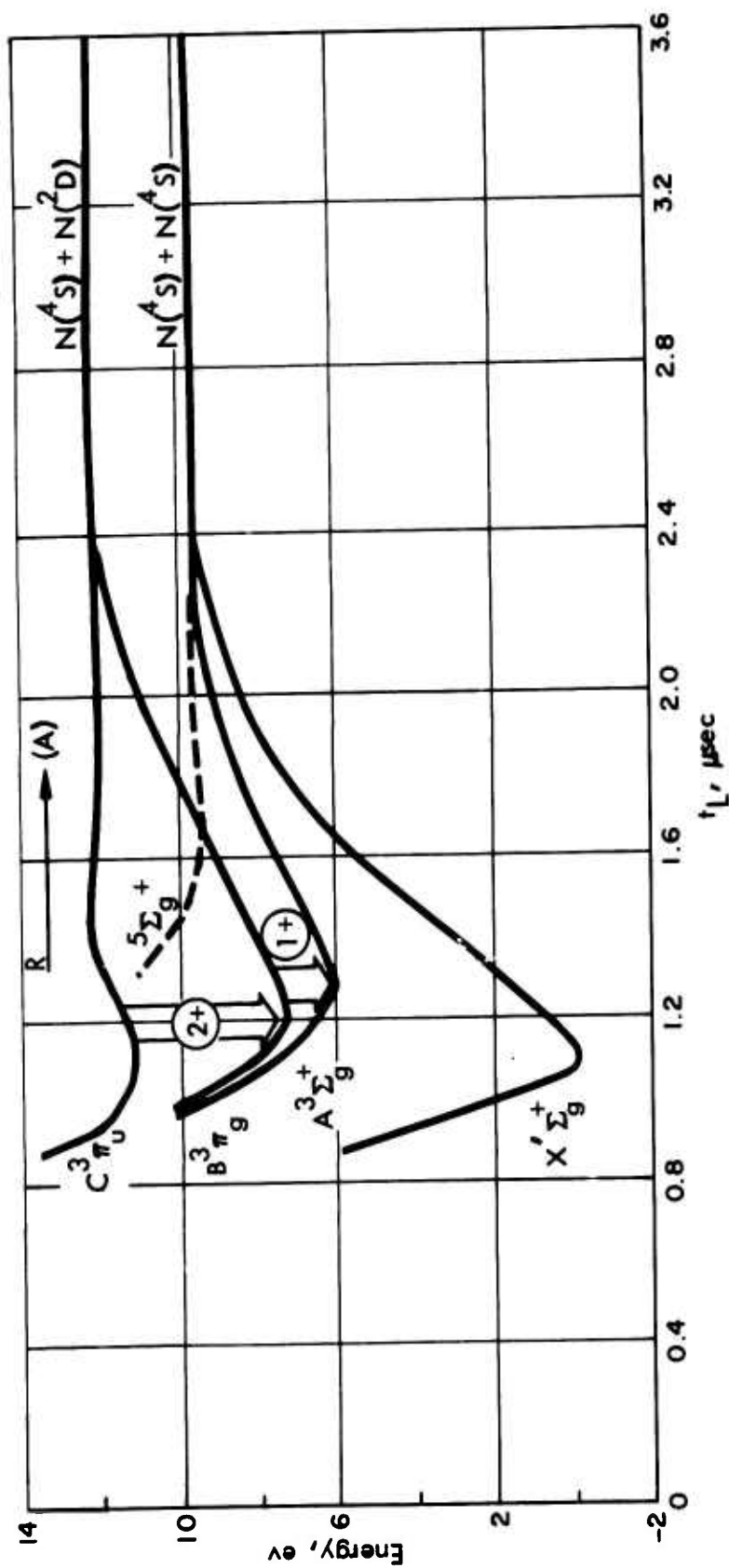
followed by the fast reaction



It is probable that for reaction (33-a) to proceed, at least one of the nitrogen atoms must be in the electronically excited 2D or 2P state.

(f) Very little is known about the NO excitation; regarding the upper state of the O_2 Schumann-Runge system, $O_2(B^3\Sigma_u^-)$, reference may be made to the preliminary work of Kivel, Hammerling, and Teare (1961) which gives a qualitative explanation of two experimental observations for the radiation observed from hypersonic shock waves in air:

1. No "overshoot" is observed in the O_2 Schumann-Runge radiation.

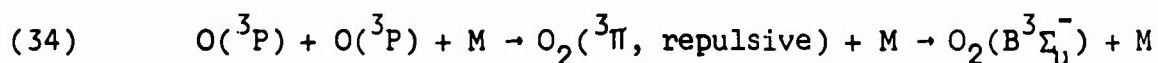


Two N atoms in the $4S$ state recombine (in presence of a third body) into the shallow $N_2(5 \Sigma_g^+)$ state, and then undergo curve crossing into the upper state of the First Positive System, $N_2(B^3 \Pi_g)$, near $v \approx 12$.

FIGURE 3 The Model of Kistiakowsky and Warneck (1957) for Excitation of the N_2 First Positive Band System

2. The radiation is not "collision limited" for pressures P_0 before the shock greater than 10^{-3} atmospheres, i.e., there are enough collisions to maintain equilibrium.

Kivel et al. postulate that the cross section for dissociation of O_2 molecules is much larger than the cross section for vibrational excitation, and also that the cross section for the process



is large. However, they do not attempt a comparison with experiment.

(g) There has been rather extensive experimentation in low-pressure flames which indicates non-thermal radiation in many cases, which is frequently due to chemi-excitation. Some representative recent results on chemi-excitation of sodium in flames are given by Hinck et al. (1965) and by Carabetta and Kaskan (1966), while chemi-excitation of CH and OH has been demonstrated by Porter et al. (1966).

VIII. EXCITATION OF ELECTRONIC STATES: A PRELIMINARY MODEL

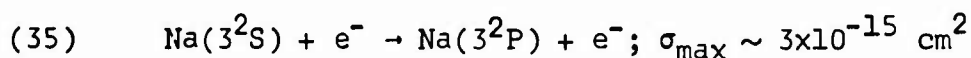
As the previous section shows, we really have no detailed overall understanding of the mechanisms for electronic excitation in a high-temperature molecular gas. However, it is possible to present a preliminary and sketchy model as follows, at least as a basis for further discussion.

In a hypersonic shock wave in a given material the bulk (or at least a significant part) of the energy goes from directed kinetic energy into some internal degree of freedom D. Then, in general, the excitation of some other internal degree of freedom E will proceed either directly from the directed kinetic energy, or else through a (D \rightarrow E) energy transfer. In other words, one can get an overall understanding by following the flow of energy between different degrees of freedom, without unraveling the intricacies of the chemistry.

Let us give some specific examples.

1. In argon, the energy goes largely into ionization; the main source of radiation is free-free radiation of electrons in the field of Ar^+ ions, which of course tracks the electron density or ionization. The line radiation from Ar^* also tracks the ionization, through processes (19) and (21) and their inverses.

2. Consider now the example of the D-line excitation in Ar with a small contamination of Na. I do not know of any measurements, but it seems clear that the $\text{Na}(3^2\text{P})$ population will be closely coupled to the ionization, largely through the fast reaction



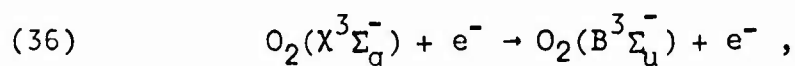
--cf. experiments of Christoph and Haft quoted in Landolt-Boernstein (1950).

3. In N_2 with an admixture of Na at relatively low shock speeds ($u_0 \lesssim 3 \text{ km/sec}$ corresponding to temperatures below 4000°K), there is very little dissociation, but the vibrational degrees of freedom are excited. The Na D-line radiation tracks the N_2 vibrational temperature --cf. Hurle (1964)--because the $\text{Na}^* - \text{N}_2(\text{v})$ coupling is fast--cf. Eq. 18 and the references quoted there.

4. In air at the shock speeds and temperatures under consideration here (or in O_2 at somewhat lower shock speeds) much of the energy goes into dissociation or "chemistry," and it does appear that most of the electronic excitation is produced by chemical reactions involving free atoms, as can be seen in Items (d), (e), and (f) of Sec. VII. However, it must be stressed that of course the statement that "electronic excitation in air is produced by chemical reactions involving free atoms" is not a solution of the problem, but rather it suggests where one should look. Because of the many different chemical reactions that are possible, it is improbable that a simple general solution exists.

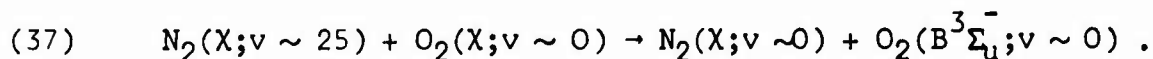
Let us be specific. The model suggests that under the conditions of Table 1, where $u_0 \sim 5$ to 7 km/sec, a large part of the energy goes into dissociation so that we should expect chemi-excitation to be an important source of radiation. Now, there are two obvious alternative methods for exciting electronic states of molecules, namely

(1) electron impact,



and

(2) vibrational-electronic energy transfer,



Process (36) or, in general, other such processes have a maximum cross section of the order of 10^{-17} to 10^{-16} cm²--cf. Bauer and Bartky (1965), which really does not allow excitation energy to be pumped fast enough through the relatively few free electrons for this to be an important process. Process (37), or some other such process, is probably very slow since it involves such a very large change in vibrational quantum number that the vibrational overlap between initial and final states will be extremely small. Further, the occupation of $N_2(X;v \sim 25)$ or some similarly highly excited state is probably rather small. In general, it seems easier to extract and transfer the energy from a completely broken bond, i.e., a dissociated molecule, than from one which is so highly excited into a discrete vibrational level that it is almost, but not quite, dissociated.

Now it is clear that these arguments are not definitive, especially since we really have no reliable cross sections for processes of the type (37). However, they do suggest that the first mechanism to investigate as a source of optical excitation is indeed chemi-excitation; the experiment should be so designed as to discriminate if possible between chemi-excitation and vibrational-electronic energy transfer.

IX. DISCUSSION

The aim of this report is to present an overall picture of our understanding of energy transfer and excitation processes in a hypersonic shock wave in air under conditions corresponding to missile or satellite reentry, i.e., shock speeds of 5 to 7 km/sec. A great deal of work has been done but many problems have not been completed, and in particular relatively little work has been done on the problem of optical excitation which provides the motivation for the present report. The report has been written in such a manner that deficiencies in our understanding of the problem should be apparent to the reader, who will then hopefully attempt to resolve them by laboratory experimentation.

Some specific discrepancies and unsolved problems are:

1. The detailed characteristics of vibrational excitation and dissociation at the higher shock speeds, taking into account impulsive collisions--cf. Miles and Shuler (1962), Rapp and Sharp (1963)--the effect of rotation--cf. Bauer and Tsang (1963)--and the possibility of vibrational excitation by chemical reaction (Bauer and Tsang, 1963).

2. The details of the chemistry at the lower temperatures where triatomic molecules and negative ions play a significant role.

3. The mechanisms for optical excitation. The very limited existing experimental work and the present preliminary model provide only a starting point from which an overall solution of this problem can be attempted.

ACKNOWLEDGMENTS

I should like to thank many people for helpful comments and discussion, in particular Drs. H.L. Mayer, J. Menkes, and H.G. Wolfhard of the Institute for Defense Analyses, Drs. R.A. Allen, C.A. Brau, M. Camac, B. Kivel, and K.L. Wray of AVCO-Everett Research Laboratory, Dr. M.H. Bortner of General Electric Co., Drs. R.E. Meyerott and W.L. Starr of Lockheed Research Laboratory, Dr. S.R. Byron of Aeronutronic, and Dr. F.R. Gilmore of RAND Corporation.

The equilibrium composition results of Tables 1 and 2 and the non-equilibrium chemistry results of Fig. 1 were run at AVCO-Everett Research Laboratory through the good offices of Dr. M. Camac.

APPENDIX A
ENERGY BALANCE IN A NORMAL SHOCK

A. INTRODUCTION

The present comments are provided as a brief summary of well-known relations. Some sources of this information are

Courant and Friedrichs (1948)	pp. 23f, 116f, 146f
Kuethe and Schetzer (1950)	pp. 131f, 167f
Hayes and Probstein (1959)	pp. 11f
Zeldovich and Rayzer (1963)	pp. 61f (of the translation)
Bond, Watson, and Welch (1965)	pp. 22f

The notations used are the following:

ρ = density

u = flow velocity

a = sound speed

e = internal energy per gram = $\int_0^T (C_v/M) dT$

h = enthalpy per gram = $\int_0^T (C_p/M) dT$

M = molecular weight

Subscript "o" refers to upstream or supersonic conditions, subscript "1" to downstream or subsonic conditions.

For an ideal monatomic gas we have

$$(A-1) \quad p/\rho = RT/M; e = (3/2) (RT/M); h = (5/2) RT/M; \gamma = C_p/C_v = 5/3$$

A "polytropic gas" is defined as one for which $e \propto T$, so that $\gamma =$ constant. The assumption of polytropicity breaks down as a result of non-ideal gas behavior, but more specifically if there is excitation of some degree of freedom above and not below some temperature (e.g., as a result of the quantum mechanical characteristics of molecular vibration), or if there is dissociation or ionization so that C_v and M are both functions of temperature and also to some extent of density.

B. CONSERVATION LAWS

The conservation laws for mass, momentum, and energy are

$$(A-2) \quad \rho_0 u_0 = \rho_1 u_1 = m$$

$$(A-3) \quad p_0 + \rho_0 u_0^2 = p_1 + \rho_1 u_1^2 = P$$

$$(A-4) \quad h_0 + \frac{1}{2} u_0^2 = h_1 + \frac{1}{2} u_1^2 = \frac{1}{2} [(\gamma + 1)/(\gamma - 1)] a_*^2$$

where

$$(A-5) \quad u_0 u_1 = a_*^2$$

C. JUMP CONDITIONS

We may define a shock strength in terms of a density ratio

$$(A-6) \quad \rho_0/\rho_1 = u_1/u_0 = \epsilon$$

and now from Eqs. (A-3), (A-4) we get the "Hugoniot condition"

$$(A-7) \quad h_1 - h_0 = \frac{1}{2} u_0^2 (1 - \epsilon^2)$$

or

$$(A-8) \quad p_1 - p_0 = \rho_0 u_0^2 (1 - \epsilon)$$

Combining these results with the equation of state, we find the complete conditions across a shock. For the case of a polytropic gas, it is possible to present the results in analytic form, as is done below; for the general situation (which is, of course, what we actually have in the present temperature range), it is necessary to use numerical results--e.g., Gilmore (1955), Feldman (1957).

D. RESULTS FOR A POLYTROPIC GAS

$$(A-9) \quad a_*^2/a_0^2 = A + B M_0^2; M_0 = u_0/a_0, \text{ initial Mach number}$$

$$(A-10) \quad A = 2 s B; B = 1/(2s + 1); \gamma = C_p/C_v = 1 + 1/s$$

$$(A-11) \quad \epsilon = A/M_0^2 + B$$

$$(A-12) \quad T_1/T_0 = 1 + M_0^2 (1 - \epsilon^2)/2s$$

$$(A-13) \quad p_1/p_0 = (1/\epsilon)(T_1/T_0)$$

For some specific examples:

$$(A-14a) \quad \text{Monatomic ideal gas, } \gamma = 1.67, A = 3/4, B = 1/4$$

$$(A-14b) \quad \text{Diatomic, polytropic gas (undissociated air, vibration not excited) } \gamma = 1.4, A = 5/6, B = 1/6$$

$$(A-14c) \quad \text{Dissociated air (very rough--See Gilmore, 1955, p. 67)} \\ \gamma = 1.15, A = 0.93, B = 0.070$$

Notice that as $M_0 \rightarrow \infty$, $\epsilon \rightarrow B$. Thus, even very large flight speeds give only very moderate increases in density, although the increases in temperature and pressure becomes very large (ratio $T_1/T_0 \sim p_1/p_0 \sim M_0^2$). The results will also hold for a general non-polytropic gas.

APPENDIX B

VIBRATIONAL RELAXATION TIMES

At room temperature, in particular, the coupling of translation and vibration is very weak because of the extreme discrepancy between a collision time, t_{coll} , and the vibrational period, t_{vib} . This point was realized very early--cf. Zener (1931); Landau and Teller (1936), and, in fact, a great deal of work has been done on vibrational relaxation times,* both experimentally and theoretically; much of this work is reviewed in the book by Herzfeld and Litovitz (1959).

Because the transition probability for translation-vibration energy transfer is small, it is customarily computed by perturbation theory, and thus the result depends very critically on the intermolecular coupling potential--e.g., Salkoff and Bauer (1959); Mies (1965). In view of the character of this coupling potential, we have very little independent knowledge of it and thus should be very careful not to overestimate the quantitative reliability of calculations of vibrational relaxation times--cf. Herzfeld and Litovitz (1959); it is the comparison with experimental values which, in fact, makes most tabulations of vibrational relaxation times useful.

*The "vibrational relaxation time" $\tau_{\text{vib}} = 1/Z P_{10} (1 - e^{-hc\omega_e/kT})$, where Z is the number of collisions experienced by a molecule per unit time and P_{10} is the probability of the ($v=1$) to ($v=0$) transition--cf. Losev and Osipov (1961).

There is one additional mechanism for vibrational excitation which avoids the "adiabatic" limitations of the conventional translational-vibrational coupling mechanism and can thus give somewhat larger transfer cross sections for molecules having incompletely filled electron shells. This proceeds through an electronic transition at a specific value of internuclear separation, the so-called process of "potential energy curve crossing"--cf. Mott and Massey (1965), pp. 351ff. The relevance of this mechanism to this problem was discovered by Nikitin (1960), who describes it as follows.

"If at least one of the colliding molecules has a singly occupied orbital, then during a collision electronic transitions are possible between states arising from the initial state which are degenerate at infinite separation of the molecules. If now the frequency of electronic transitions and of the vibrations are equal, there arises a peculiar resonance which brings about a relatively large cross section for the excitation of the vibrations."

Nikitin (1960) suggested that this mechanism would be important for NO, and Wray (1962) showed that the experimental observations in NO can be explained to high temperatures by a combination of the conventional Landau-Teller and the Nikitin mechanism, treated in a somewhat heuristic manner.

However, it should be noted that at the high temperatures of interest here all these analyses tend to break down. The kinetic energy of the incident molecules is so high that, in fact, the coupling of translation and vibration is much better than would be predicted by the simple "adiabatic" theory of Landau and Teller (1936).

The reason for this is that whereas at room temperature for almost all collisions we have

$$(B-1) \quad t_{\text{coll}} \gg t_{\text{vib}} \quad (T \sim 300^{\circ}\text{K})$$

so that the translation-vibration coupling is weak and the Landau-Teller (1936) model applies, yet at $T \sim 6000^{\circ}\text{K}$ (~ 0.5 ev) for many collisions we have

$$(B-2) \quad t_{\text{coll}} \sim t_{\text{vib}} \quad (T \sim 6000^{\circ}\text{K})$$

and under these conditions the transfer of energy between translation and vibration becomes quite efficient. Very little work has been done as yet on these "impulsive collisions"--cf. Mies and Shuler (1962); Rapp and Sharp (1963).

There is yet another mechanism which may lead to vibrational excitation, in particular at high temperatures. This is provided by chemical reactions involving atoms which lead to vibrationally excited products--cf. Bauer and Tsang (1963). Thus far, nobody appears to have followed up the suggestion of Bauer and Tsang (1963) to see how important this mechanism actually is.

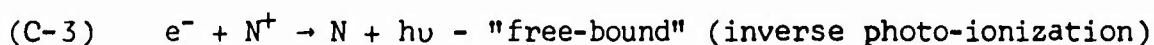
It should be noted that there is some experimental evidence to indicate that indeed vibrational excitation is much more efficient at higher temperatures ($T \gtrsim 4000^{\circ}\text{K}$ for air) than at room temperature. This can be inferred from measurements such as those on shock structure in oxygen due to Wray and Freeman (1964), which are referred to in Secs. III and IV.

APPENDIX C
SOME COMMENTS ON RADIATION FROM HIGH-TEMPERATURE AIR

In the temperature range below 8000°K , the main radiation from equilibrium air comes from the six molecular electronic transitions which are listed in Table C-1. There is also radiation in the near infrared from the NO vibration-rotation bands, and from the recombination process--cf. Fontijn, Meyer, and Schiff (1964).



At higher temperatures ($\geq 12,000^{\circ}\text{K}$) where there are no molecules and the gas is largely ionized, the radiation is due to line radiation from excited atoms and ions, and to the free-free and free-bound continua, such as



In fact, at the lower temperatures, say, $T \lesssim 8000^{\circ}\text{K}$, where there are significant numbers of molecules, there is a drastic difference between the radiation from different chemical species. Once the gas is largely ionized the predominant free-free continuum is only weakly dependent on the chemical species present, since it depends largely on the electron density and the temperature.

Table C-1 -- MAJOR RADIATING BAND SYSTEMS IN AIR

<u>Band System</u>		<u>$\lambda_{00}(\text{\AA})^a$</u>	<u>f_{abs}^b</u>
N_2 ($\text{B}^3\Pi_g - \text{A}^3\Sigma_u^+$) ^c	First Positive	6190	0.0028
N_2 ($\text{C}^3\Pi_u - \text{B}^3\Pi_g$) ^d	Second Positive	4330	0.043
N_2^+ ($\text{B}^2\Sigma_u^+ - \text{X}^2\Sigma_g^+$)	First Negative	3930	0.035
O_2 ($\text{B}^3\Sigma_u^- - \text{X}^3\Sigma_g^-$)	Schumann-Runge	2020	0.17 - 0.34 $\lambda/10^4$
NO ($\text{B}^2\Pi_r - \text{X}^2\Pi_r$)	Beta	2190	0.0053
NO ($\text{A}^2\Sigma^+ - \text{X}^2\Pi_r$)	Gamma	2250	0.0025

^aWavelength of the $v = 0$ to $v = 0$ vibrational band.

^bOscillator strength of the whole system, measured in absorption--cf. Main and Bauer (1966) for references.

^cThe $\text{N}_2(\text{A}^3\Sigma_u^+; v = 0)$ state is 6.2 ev above the $\text{N}_2(\text{X}^1\Sigma_g^+; v = 0)$ ground state.

^dThe $\text{N}_2(\text{B}^3\Pi_g; v = 0)$ state is 7.3 ev above the $\text{N}_2(\text{X}^1\Sigma_g^+; v = 0)$ ground state.

It is of some interest to discuss briefly why air is not a strong radiator in the temperature range below $12,000^{\circ}\text{K}$. At room temperature, of course, air has a window to solar radiation, i.e., to the wavelengths covering 90 percent of the energy output from a 5500°K blackbody. Specifically, there is a ultraviolet cutoff at 3000 \AA which arises from ozone. The infrared cutoff arises largely from vibrational band systems of the minor species CO_2 and H_2O and from some forbidden transitions of O_2 . The key point here is that molecular nitrogen, the main constituent of air, has no optically allowed transitions to or from the ground state, requiring 6.2 eV of excitation.

At temperatures of the order 0.5 eV ($\approx 6000^{\circ}\text{K}$), the O_2 Schumann-Runge band system shifts somewhat in frequency and becomes important in the violet, while the NO molecule, which is formed at elevated temperatures up to a maximum equilibrium mole fraction of several percent, has several allowed transitions into the ground state and is thus a relatively important source of radiation and absorption. The N_2 molecule also becomes a more important radiator at elevated temperatures where the occupation of the $\text{B}^3\pi_g$ and $\text{C}^3\pi_u$ levels is not completely negligible. Nevertheless, air is simply not an important radiator in the visible at temperatures below 1 eV, certainly not in comparison with CO_2 violet ($\text{B}^2\Sigma^+ - \chi^2\Sigma^+$) and red ($\text{A}^2\Pi_1 - \chi^2\Sigma^+$) band systems, among others.

The discussion of radiation from air and other gas-phase systems in the molecular temperature range of $2000^{\circ}\text{K} \lesssim T \lesssim 10,000^{\circ}\text{K}$ is quite complex and will not be taken up here in detail. Reference may be

made to the work on "opacity" of Kivel, Mayer and Bethe (1957), Keck et al. (1958), Armstrong et al. (1961), and Main and Bauer (1966), among others.

As a historical note, it may be mentioned that when people first got concerned with the reentry of hypersonic vehicles into the atmosphere in the early and mid 1950's there was considerable interest in the radiative properties of high temperature air because it was felt that radiative heating might be a significant part of the total aerodynamic heat load. In those days, it was not known that the absolute intensities or f-numbers of molecular band systems are indeed of the order 10^{-3} to 10^{-2} , rather than of order one as for atomic transitions.* The early experimental work which was carried out largely at AVCO-
Everett Research Laboratory--Kivel, Mayer, and Bethe (1957); Keck, Camm, Kivel and Wentink (1959)--showed that in fact the f-numbers of the band systems of importance in high-temperature air are so low that radiative heating is unimportant for terrestrial satellite reentry. However, at higher speeds and in particular for the Martian atmosphere which is composed of CO_2 , N_2 , and argon, radiative entry heating does indeed become a problem.

*The reason why molecular f-numbers for electronic transitions in the visible are so low is that--analogous to the atomic case--most of the effective radiative intensity lies in the high-lying Rydberg transitions.

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<p>This report surveys our present (and very limited) understanding of the mechanisms for electronic excitation in a hypersonic shock wave in air. To do this, we review the overall mechanisms of energy flow between translational, rotational, vibrational, chemical, and electronic degrees of freedom in a shock wave. Particular stress is placed on those aspects of the problem which are not well understood; namely, the mechanism for vibrational excitation and dissociation in high-speed shocks in which the assumptions of weak translation-vibration coupling and dissociation by vibrational ladder-climbing, which apply at room temperature, breakdown. While one can write a set of rate constants for at least the major chemical reactions in air, there is no comparable information on the excitation of electronic degrees of freedom in high-temperature air, and our knowledge of mechanisms is very limited. For illustrative purposes, the case of a shock wave in argon is reviewed.</p> <p>As an interim working model, it is suggested that the excitation of degrees of freedom, which contain only a small fraction of the energy, goes by way of those degrees of freedom which contain a large fraction of the energy. In the case of air for shock speeds of the order 7 km/sec, this is dissociation, or "chemistry," and thus it is suggested that most of the excitation is chemical in nature, just as ionization is produced by the "chemical" process of inverse dissociative recombination. Present data are consistent with this picture, but further experimental work is needed both to confirm it and also to make it specific and quantitative.</p>		

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